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ABSTRACT

It is demonstrated that the temperature dependence of the resistivity of $Qn(TCNQ)_2$ and $Ad(TCNQ)_2$ is similar and is distinctively different from that observed in NMeP-TCNQ.

KIVONAT

Demonstráljuk, hogy a $Qn(TCNQ)_2$ és $Ad(TCNQ)_2$ ellenállásának hőmérsékletfüggése hasonló, de határozottan különbözik az NMeP-TCNQ-n megfigyelttől.

АННОТАЦИЯ

Показано, что температурная зависимость сопротивления $Qn(TCNQ)_2$ и $Ad(TCNQ)_2$ имеет одинаковый характер, но разко отличается от температурной зависимости, наблюдаемой на NMeP--TCNQ-n.

High temperature resistivity of $Qn(TCNQ)_2$ and $Ad(TCNQ)_2$

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It is demonstrated that the temperature dependence of the resistivity of $Qn(TCNQ)_2$ and $Ad(TCNQ)_2$ is similar and is distinctively different from that observed in NMeP-TCNQ.

The complex salts of tetracyanoquinodimethane with quinolinium and acrinidium ($Qn(TCNQ)_2$ and $Ad(TCNQ)_2$ respectively) are representatives of the highly conducting TCNQ compounds (Shchegolev 1972) characterized by a smooth maximum in the conductivity somewhat below room temperature. Various explanations have been envisaged to account for this behaviour, i.e. a metal-insulator transition with a single particle gap going to zero with increasing temperature (Coleman et al 1973), variable range hopping between states localized by disorder effects (Bloch et al 1972) and chain end limited resistivity due to the finite length of the conducting chains (Ehrenfreund et al 1972). The overall features of the conductivity: the activated behaviour at low temperatures together with the flattening off at a certain temperature are well explained by all this models requiring a more careful analysis.

We have performed detailed resistivity measurements on $Qn(TCNQ)_2$ and $Ad(TCNQ)_2$ in the high temperature region to try to distinguish between these explanations. Our results strongly suggest the existence of a mobility gap separating localized and extended states, the gap is smeared out by thermal fluctuations, at hight temperatures.

$Ad(TCNQ)_2$ and $Qn(TCNQ)_2$ were prepared from high purity starting materials according to the procedure of Melby et al (1962). Needle like $Qn(TCNQ)_2$ crystals of 3...5 mm length were obtained after reaction, $Ad(TCNQ)_2$ single crystals of appropiate size were grown from acetonitrile solution. The resistivity was measured by four probe method. In order to avoid inhomogenous current injection care has been taken to cover fully the ends of the crystals with the contact paint. The resistance was recorded contrinuously and occasional cracking of the crystals observed in some cases was evident from a sudden jump of the resistance. The high temperature resistivity is shown in Fig. 1. for both compounds. We have found no differences in the magnitude and temperature dependence of the resistivity of different crystals within the measuring accuracity (limited by the evaluation of sample dimensions). The resistivity however increased slighly for both compounds, presumably due to sublimation, when the sample was heated above $100^{o}C$.

The good reproducibility of the resistivity from sample to sample confirms that chain end effects have only a minor role. In case of conducting chains having a low resistance,

the current flow is blocked by the barriers at chain ends and then large variations from sample to sample are expected, and observed in TTF-TCNQ where this situation is appropriate (Cohen et al 1974). On the other hand, when phonon assisted hopping occurs between a network of parallel chains, the resistivity is determined by the average chain length L which is expected to be the same for crystals obtained by the same procedure. In this case however the resistivity should decrease with decreasing chaing length (Maschke et al 1974). This is contrary to what is observed in overheated samples, if we accept the plausible assumption that sublimation reduces the average chain length. We believe therefore that chain ends do not affect the measured resistivity and $\rho(T)$ is characteristic to a scattering process within the TCNQ chains.

The similar behaviour of the two salts is apparent and is shown in more detail in Fig. 2, where ρ/ρ_{min} is plotted versus T/T_c where T_c the temperature of the resistivity minimum. We also note that the activation energies ΔE obtained in the low temperature region (0.022 eV and 0.03 eV for $Ad(TCNQ)_2$ and $Qn(TCNQ)_2$ respectively) scale with the same factor as T_c. The main features of the resistivity behaviour are: a./ a minimum at temperature T_c corresponding to about $0.6\ \Delta E/k_B$, and b./ the resistivity is proporcional to the temperature well above T_c. This behaviour should be contrasted to that found in NMeP-TCNQ which shows a similar overall

behaviour but with $T_c \sim 0.5\ \Delta E/k_B$ ($T_c \sim 250^oK$ and $\Delta E \sim 0.047$ eV) and $\rho(T) = A + B\ T^4$ at high temperatures (Coleman et al 1973). Thus in parallel to important differences in the magnetic properties, the resistivity is also different for NMeP-TCNQ and the complex TCNQ salts.

The magnitude of the resistivity is much smaller than that corresponding to phonon assisted hopping between localized states. At high temperatures hopping is confined to nearest neighbours and the maximum conductivity should not exceed the value of the order of $1\ \Omega^{-1}cm^{-1}$ (Mott and Davis 1972).

The hopping model disagreas also with the high temperature slope of the resistivity, for in the diffusive region (Bloch et al 1972)

$$\rho(T) = \frac{k_B T}{N_{eff}\, e^2 a^2 \nu_f}$$

and $\partial\rho/\partial T = 1.2\ 10^{-3}\ \frac{\Omega cm}{^oK}$ for a = 3.2 Å, $\nu_f = 10^{-12}\,sec^{-1}$ and $N_{eff} = 1$ orders of magnitude to small to account for the experimental temperature dependence $\partial\rho/\partial T = 3\ 10^{-5}\,\Omega$ cm/^oK. This confirms that conduction is due to extended electron states, and then the activation energy observed below the maximum reflect the contribution of electrons excited across a mobility gap.

The relation $\rho \sim T$ observed in $Ad(TCNQ)_2$ in a broad temperature region is characteristic to a mobility gap smeared out by thermal fluctuations, together with a strong scattering

process. Although electron-phonon interaction accounts for the linear temperature dependence well above the Debye temperature with a large electron-phonon coupling constant (Holstein 1954), we mention that electron-electron interactions together with polaronic effects can also describe the observed temperature dependence (Holczer 1975).

This analysis suggest a gap in the single particle excitations in case of quarter filled band appropriate for the 1:2 salts. The band gap is expected to arise from long range Coulomb forces in Mott's sense and can also be obtained from a model taking into account nearest neighbour Coulomb interactions (Ovchinnikov 1973, Holczer 1975). The existance of the band gap associated with a singlet ground state has also been recently demonstrated by susceptibility measurements (Miljak et al 1975). Static disorder due to the asymmetric donor molecules gives rise to a tailing into the Hubbard gap and turns the sharp band gap into a mobility gap. The effect of band tailing and the contribution of the localized states to the dc conductivity is unimportant at high temperatures, however they may have a dominant role at low temperatures and at finite frequencies similarly to that observed in amorphous semiconductors.

We conclude by noting that this picture is not in conflict with the exact theorem that all sates are localized in one dimension (see for example Shchegolev 1972) for in

case of strong electron-phonon or electron-electron interactions and of weak random potentials the phase coherence is destroyed by interaction effects before the exponential decay of the wave function becomes effective. Both localized and delocalized states can exists under such circumstances in the same sense as discussed by Economu and Cohen (1972).

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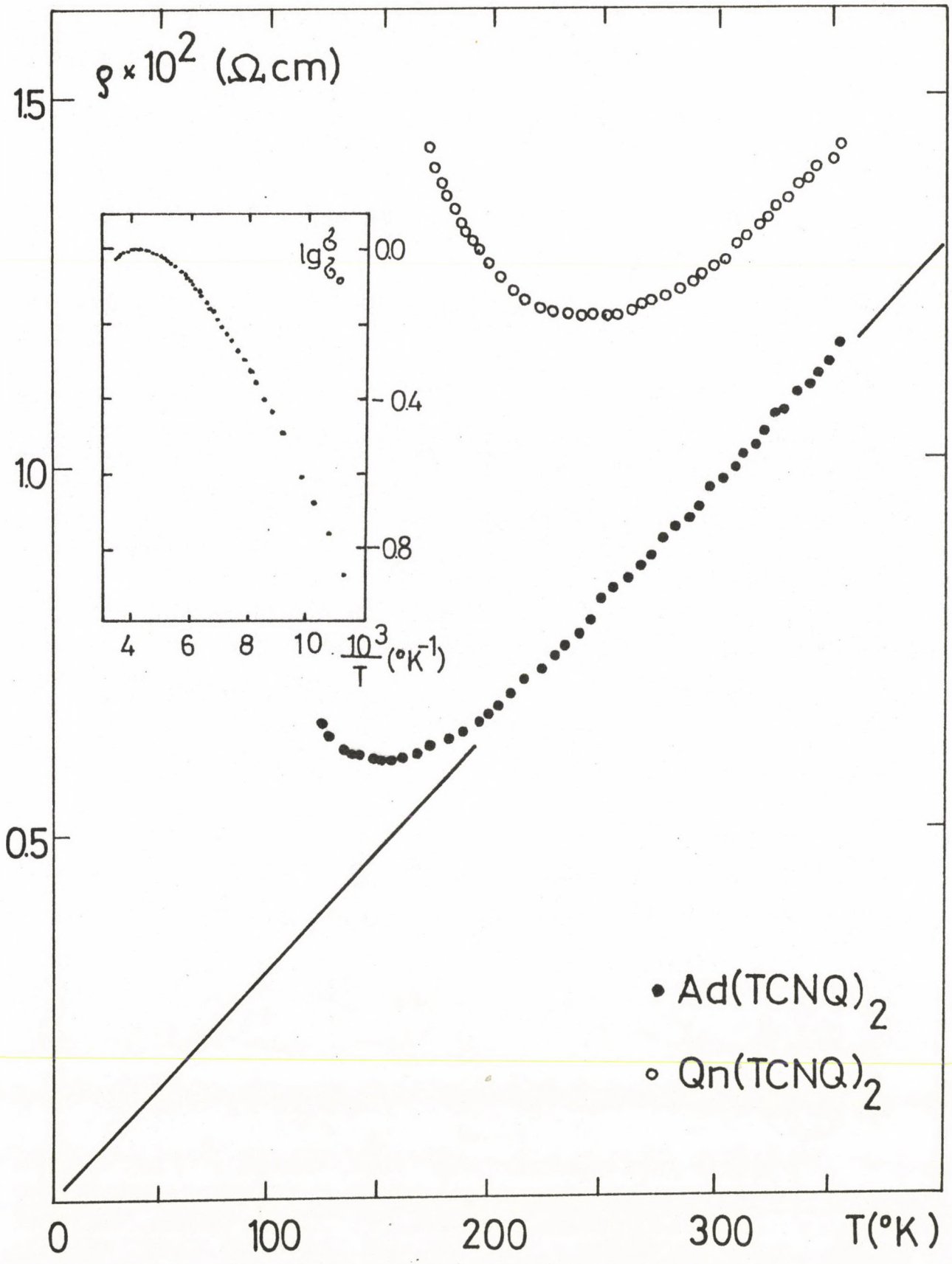

ρ × 10² (Ω cm)
1.5
1.0
0.5
0
100
200
300
T(°K)
lg σ/σ₀
0.0
0.4
0.8
4
6
8
10
10³/T (°K⁻¹)
• Ad(TCNQ)₂
∘ Qn(TCNQ)₂

Fig. 1.

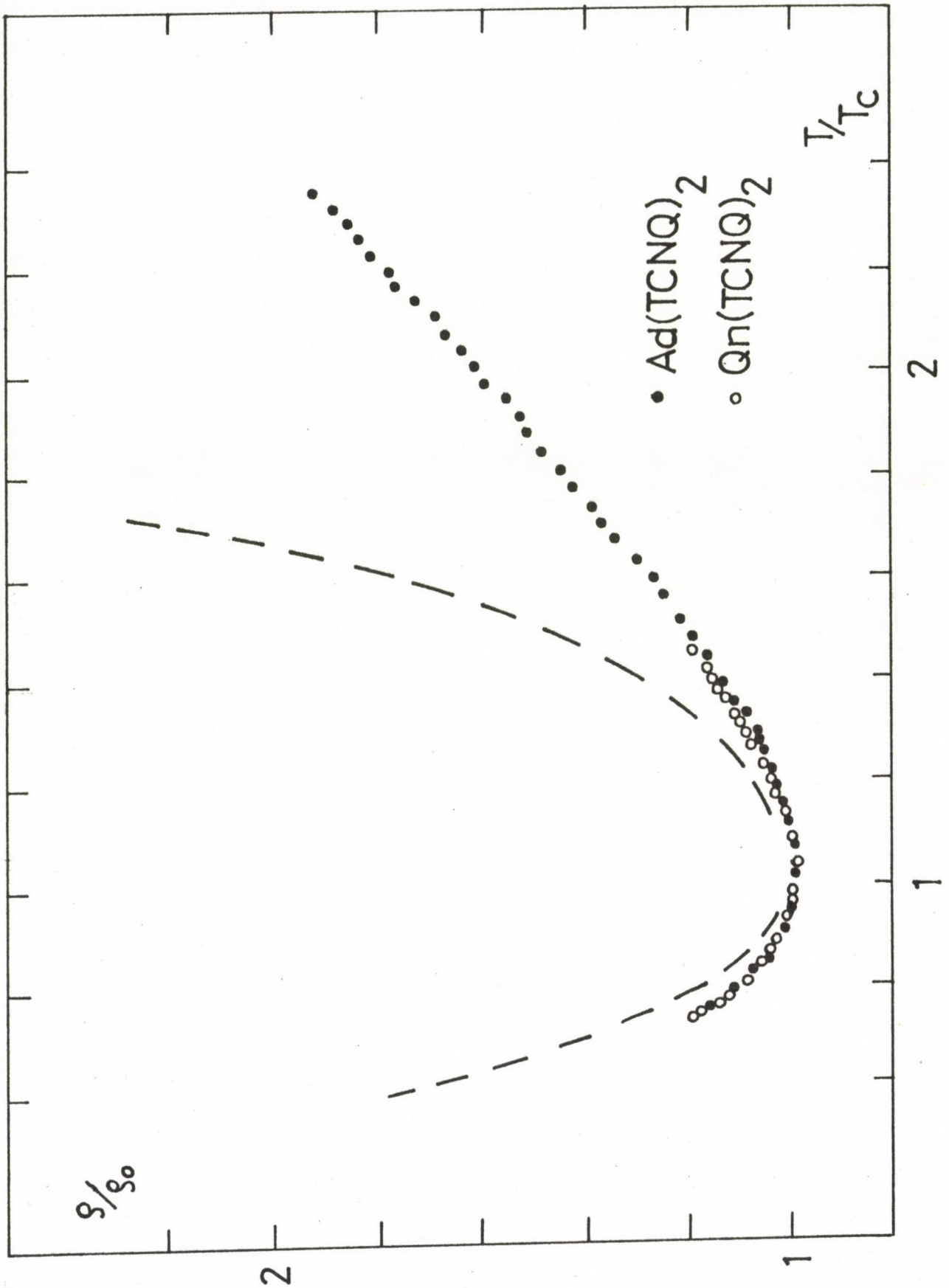
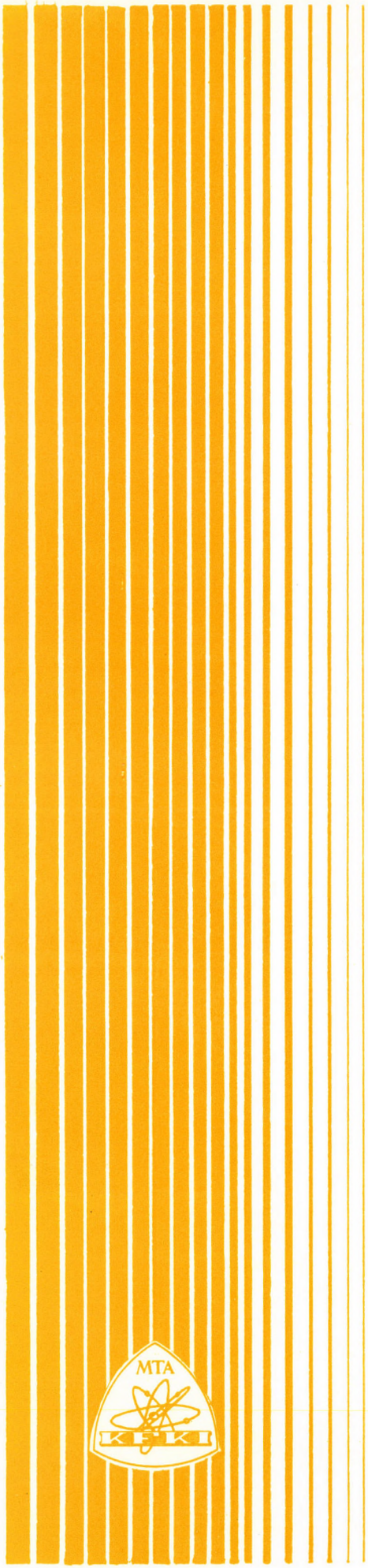


Fig.2.



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